OFFICE OF NAVAL RESEARCH

FINAL TECHNICAL REPORT

For the Symposium

PHYSICAL CHEMISTRY OF SOL-GEL MATERIALS

Held during the

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AMERICAN CHEMICAL SOCIETY
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On Behalf of:
Division of Physical Chemistry, American Chemical Society
(Sponsoring Organization)

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1. OBJECTIVES OF THE SYMPOSIUM

The sol-gel process is a chemical synthesis technique for preparing oxide gels, glasses and inorganic compounds at far lower temperatures than is possible by conventional synthesis methods. In recent years, the sol-gel process has emerged as a convenient, non-melting approach for synthesizing amorphous inorganic solids with designed properties. Not only is it possible to prepare a wide range of oxides, the flexible solution chemistry enables one to incorporate a large variety of organic, organometallic or biological molecules in the inorganic oxide matrix. In addition, there is the opportunity to synthesize organic/inorganic hybrid materials which consist of an inorganic network in intimate contact with an organic component. This approach, which is being widely investigated, provides an opportunity to design novel materials with both inorganic and organic characteristics. Finally, it is possible to use the sol-gel method to produce materials with tailored microstructures ranging from highly porous, high surface area aerogels with $< 1\%$ solids, to fully dense materials.

There are numerous examples of where physical chemistry has had a significant impact on the development of the sol-gel field. NMR has been widely used to monitor the hydrolysis and condensation reactions and continues to the present day to develop new insights into local chemistry and bonding. X-ray and neutron techniques have been of central importance in understanding the nature of structural development of the inorganic network. The preparation of high surface area aerogels has led to a new family of materials whose surface properties are capable of dominating the electrochemical behavior of solids. Optical spectroscopy has been used extensively to study intramolecular properties, dynamics and confinement effects of molecules encapsulated in the sol-gel matrix.

The objective of the symposium on the Physical Chemistry of Sol-Gel Materials was to bring together scientists from both the sol-gel field along with experts in the various measurements and theoretical areas whose interests extend to sol-gel science. Despite the vital role of physical chemistry studies in the sol-gel field, most sol-gel symposia emphasize synthetic issues. This symposium, sponsored by the Physical Chemistry Division of the American Chemical Society, was, to the best of our knowledge, the first one to be directed at the underlying physical chemistry. The invited speakers were a group of distinguished individuals whose research on sol-gel materials best illustrated the underlying physical chemistry of sol-gel derived materials.

The following section provides a brief overview of the symposium and identifies some of the more significant topics presented. A summary of the individuals receiving support is included. This report also contains three appendices. Appendices I and II list the

authors and titles of the oral presentations and posters, respectively. Appendix III contains the abstracts for all 56 papers in the symposium.

2. SYMPOSIUM HIGHLIGHTS

The symposium generated considerable response from the physical chemistry and sol-gel communities. There were a total of 6 sessions that were held over four consecutive days. There were a total of 32 oral presentations, of which 24 were invited. The fact that over 80% of our invitations were accepted is a clear indication of the interest in the field. In addition there were 24 posters presented at the evening poster session.

The first day of the meeting was devoted to providing a review of pertinent aspects of the sol-gel field, including emerging directions. These opening sessions were comprised of speakers who are widely recognized in the field. Their presentations were, to a large extent, designed to provide the background for the specific topics presented on the succeeding days. One theme which emerged was that of mesoporous materials; the thermodynamics of formation and the physical chemistry of the nanodimensional structures (Brinker, Stucky, Chmelka).

The series of specialized sessions began on the second day of the symposium. Highlights of the session of Biomolecular Sol-Gels included fundamental optical studies of biomolecules encapsulated in sol-gel matrices (Bright), stability and reactivity issues (Kostic) and the unique transformation properties of encapsulated heme proteins (Friedman). The session on Ion and Molecular Transport was the best attended of all the sessions. The key talks during this session included the electrochemical properties of sol-gel electrodes (Lev) and aerogels containing nanodimensional phases (Rolison). The ability to use the sol-gel process to prepare transparent materials with specific dopants is one reason that the optical properties of these materials are widely investigated. The session on Optical Studies was representative of this range of topics as the papers included subjects covering excitation phenomena (Prasad), charge transfer (Meyer) and morphology effects (Leventis). Highlights of the final oral session, Dynamics and Structural Considerations, included the confinement of molecules in small pores (Chronister), the dynamics of confined liquids (Jonas), neutron diffraction studies (Merzbacher) and the influence of high pressure on mesoporous materials.

The poster session underscored the diversity of the symposium. For the most part, the posters provided an opportunity for graduate students, post-doctoral scholars and junior faculty to showcase their research. The 24 posters was well above the 'critical mass' necessary to have a vibrant poster session. As is the case with most poster sessions, the energy and enthusiasm of these impressive young investigators made for a splendid session.

3. DISTRIBUTION OF FUNDS

The ONR support was used to finance the conference registration and travel expenses for selected individuals who presented either invited or contributed talks at the symposium. Priority was given either to junior faculty, young research scientists or faculty coming from colleges and smaller universities as these individuals have modest research programs and limited resources available. Each of the following individuals received $400 support:

Sarah Tolbert	James Cox	John Fourkas
Bakul Dave	Esther Lan	Joel Friedman
Nenad Kostic	Al Stiegman	Nick Leventis
Gerald Meyer		

APPENDIX I: Schedule of Oral Presentations

SUNDAY MORNING, March 21: *Sol-Gel Materials*

Title of Paper	Author(s)
New Directions in Sol-Gel Processing: Self-Organized Micro- and Mesostructured Media	C.J. Brinker, F. van Swol, L. Frink, Y. Lu, H. Fan, N. Huesing, A. Sellinger and D. Doshi
Solid-state NMR Characterization of Sol-Gel Derived Organically Modified Silicates	Florence Babonneau
The Biogenesis and Cooperative Assembly of Complex Materials	G.D. Stucky et.al.
Relevance of Physical Chemistry to Development of Sol-Gel Derived Products	J. D. Mackenzie and E. Bescher

SUNDAY AFTERNOON, March 21: *Organic/Inorganic Sol-Gels*

Title of Paper	Author(s)
Hierarchically Ordered Inorganic-Organic Composites and Porous Oxides	B.F. Chmelka, S.C. Christiansen, M.D. Mann, N.A. Melosh, P. Schmidt-Winkel, P.Yang, D. Zhao, G.D. Stucky
Sol-Gel Polymerization of Organotrialkoxysilanes. Effect of the Organic Substituent on Gelation	D.A. Loy, B.M. Baugher, D.A. Schneider,
Sol-Gel Process in 2-dimensions	R.M. Leblanc, S. Vidon S.Wang
Surface Area, Porosity and Pyrolysis of Inorganic/Organic Hybrid Gels Derived from Polycarbosilanes	L. V. Interrante, Q. Liu G. Soraru
Organic/Inorganic Molecular Hybrid Materials By Reverse Sol-Gel Processing	R.M. Laine, L. Viculis, M.Z. Asuncion, H. Cheng, R. Narayanan

MONDAY MORNING, March 22: ***Biomolecular Sol-Gels***

Title of Paper	Author(s)
Stabilization of Oxidases in Silica Xerogels	Q. Chen, A.Heller, J. Heller, G. Kenausis
Probing the Behavior of Biomolecules Sequestered within Sol-Gel Derived Glasses	F.V. Bright, G.A. Baker, M.A. Doody, S. Pandey, N.J. Bonzagni, C.M. Crago.
Interactions of Biological Molecules with Sol-Gel Glasses	B.C. Dave
Immunoassays for Detection of Trinitrotoluene using Sol-Gel Silica Glasses	E.H. Lan, B. Dunn, J.I. Zink
Activation Parameters of a Xerogel Encapsulated Enzyme/Substrate System Immersed in Supercritical Carbon Dioxide	B.C. Dunn, T.A. Cutler, C.R. Lloyd, E.M. Eyring.
Dynamics and Reactivity in Sol-Gel Encapsulated Proteins	J.M. Friedman, T.K. Das, D.S. Gottfried, L.J. Juszczak, I. Khan, E.S. Peterson, D.L. Rousseau, C. Shannon, U. Samuni
Special Effects of Glass Matrices on Protein Conformation, Uptake Equilibrium, and Catalytic Activity	J. Badjic, E.N. Kadnikova, N.M. Kostic

MONDAY AFTERNOON, March 22: ***Ion and Molecular Transport***

Title of Paper	Author(s)
Recent Advances in the Electrochemistry of Sol-Gel Derived Silicates and Organically Modified Silicates	O. Lev, S.Bharathi, S. Sampath, J. Gun, L. Rabinovich.
Matrix Effects on Electrochemical Reactions in Sol-Gel Materials	J. A. Cox
The Physical and Chemical Properties of Silica Aerogels Paved with Nanowires	D.R. Rolison, J.V. Ryan, C.I. Merzbacher, J.W. Long, M.L. Anderson
New Template Approach to Production of Ultra-high Surface Area Lithium Intercalation Materials	D.A. Buttry, E. Shoji

TUESDAY MORNING, March 23: ***Optical Studies***

Title of Paper	Author(s)
Molecules and Charges at the Aqueous Interface of Microscopic Particles: Polymer beads, Emulsions, Semiconductors, and Liposomes	K.B. Eisenthal, Y. Liu, E. Yan, D. Zimdars, J. Dadap, A. Srivistava, X. Zhao, S. Ong, H. Wang.
Optical Excitation and Dynamics in Sol-Gel Derived Nanostructured Materials	P.N. Prasad, A. Biswas, C. Friend, J. Swiatkiewicz, M. Lal, G. Manohala,
Stabilization of Ru(II) Polypyridyl Compounds in Mesoporous Sol-Gel Processed Titanium Dioxide Films	P. Qu, C.A. Kelly, D. Thompson, F. Farzad, G.J. Meyer
Metal Activator-Free Silicate Phosphors	M.J. Sailor, W.H. Green, M.A. Ansell
Long-Lived Luminescent Defect Sites in Pure Silica Xerogels	A.E. Stiegman, A.S. Soult
Synthesis and Characterization of Silica Aerogel Monoliths Bulk-Modified with Covalently Bound 2,7-Diazapyrenium Moieties	N. Leventis, I. Elder, D. Rolison, C. Merzbacher

WEDNESDAY MORNING, March 24: ***Dynamics and Structural Characterization***

Title of Paper	Author(s)
The Structure and Dynamics of Sol-Gel Glasses by Time-Resolved Optical, Spectral Hole-Burning, Gas Adsorption Isotherm, and Neutron Diffraction Studies	E.L. Chronister, P. Lloyd
Orientational Dynamics of Liquids Confined in Nanoporous Sol-Gel Glasses	J.T. Fourkas, B.J. Loughnane, R.A. Farrier, A.S. Scodinu
Dynamic Structure of Liquids in Nanoporous Glasses	J. Jonas
Magnetic Relaxation Dispersion Studies of Liquids in Confined Environments	R.G. Bryant, J.-P. Korb
Structural Characterization of Porous Nanophase Materials by Contrast-Matching SANS	C.I. Merzbacher, D.R. Rolison, M.L. Anderson, V.M. Cepak, K.E. Swider

APPENDIX II: Complete Listing of Posters

WEDNESDAY EVENING, March 24: ***Poster Session***

Raman study of liquid methyl iodide confined in porous silica xerogel monoliths: Autoregressive band shape analysis.	E. L. Quitevis, R. E. Wilde, T. R. Bryans
Temperature-dependent rotational dynamics of carbon disulfide confined in nanoporous glasses.	B. J. Loughnane, J. T. Fourkas
Effects of the reaction medium on oxidation of organic substrates catalyzed by peroxidases in sol-gel glass.	E. N. Kadnikova, N. M. Kostic
Unfolding of bovine carbonic anhydrase II entrapped in sol-gel glass.	J. Badjic, N. M. Kostic
Molecular imprinting in guanidine functionalized sol-gel materials.	D. Y. Sasaki, T. M. Alam, R. A. Assink, B. Hart, K. J. Shea
Influence of surface area on the electrochemical properties of sol-gel derived transition metal oxides.	W. Dong, J. H. Harreld, B. S. Dunn
A sol-gel approach to rigid well-defined thin films.	J. H. Rouse, B. A. MacNeill, G. S. Ferguson
Smart glasses: Environmental sensitivity of a novel organically-modified silica sol-gel.	M. S. Rao, B. C. Dave
Design of novel solid state biocatalysts by sol-gel encapsulation of enzymes.	R. Obert, B. C. Dave
Sol-gel synthetic routes to novel lithium ion intercalation materials.	K. C. White, D. A. Buttry, R. E. Torresi, S. Torresi
Synthetic control over the fabrication of homogeneous vanadia-silica xerogels	A. E. Stiegman, M. D. Curran
Synthesis and ultrafast electronic relaxation dynamics of PbI_2 colloidal nano-particles.	J. Z. Zhang, A. Sengupta
Impeded rotation of a protein in a sol-gel matrix	D.S. Gottfried, A. Kagan, J.M. Friedman

WEDNESDAY EVENING, March 24: ***Poster Session***

Dynamics of curved DNA molecules in polyacrylamide gel	U. Mohanty
Concentration effects on the morphology of co-precipitated mixed metal oxalates.	K. F. Schoch, C. J. Painter, T. R. Vasilow
Dendrimer/sol-gel composites: Towards solution-phase chemical sensing.	P. J. Skrdla, S. S. Saavedra, R. M. Crooks, N. R. Armstrong
Comparative study of ZnO nanoparticles prepared by sol-gel, reverse micelle and laser vaporization techniques.	M. S. El-Shall, S. Li, I. N. Germanenko
Photoluminescence quenching of silicon nanocrystals by electron acceptors.	M. S. El-Shall, S. Li, I. N. Germanenko
Effects of framework structure on the phase stability of mesophase silica/surfactant composites.	A. F. Gross, E. J. Ruiz, S. H. Tolbert
Alignment and isolation of semiconducting polymer in the nano-pores of an ordered silica matrix.	J. Wu, A. F. Gross, S. H. Tolbert
High pressure effects on ordered surfactant/inorganic mesophase composites.	J. Wu, X. Liu, S. H. Tolbert
Spectroscopic characterization of CdS nanoparticles with different capping environments.	B. Zou, R. Little, J. Wang, M. A. El-Sayed
In-situ probing by fluorescence spectroscopy of the formation of continuous highly-ordered lamellar phase mesostructured thin films.	M. Huang, B. S. Dunn, H. Soyez, J. I. Zink
A supramolecular machine in the solid state.	S. Chia, J. I. Zink, J. F. Stoddart

APPENDIX III

SYMPOSIUM ABSTRACTS

PHYSICAL CHEMISTRY OF SOL-GEL MATERIALS

213th National Meeting of the
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007. NEW DIRECTIONS IN SOL-GEL PROCESSING: SELF-ORGANIZED MICRO- AND MESOSTRUCTURED MEDIA. C.J. Brinker, F. van Swol, L. Frink, Y. Lu, H. Fan, N. Huesing, D. Doshi, T. Ward and P. Weiss, The University of New Mexico/Sandia National Laboratories Advanced Materials Lab, 1001 University Blvd. SE, Albuquerque, NM, and Alan Sellinger, Canon Research Center America, Inc., 4009 Miranda Ave., Palo Alto, CA 94304

Sol-gel processing has emerged as the preferred route to prepare a variety of highly organized porous and composite materials. This talk will present a brief overview of "classical" sol-gel processing followed by a discussion of new approaches that combine sol-gel processing with various templating and self-assembly strategies, enabling control of pore size and pore connectivity and offering the possibility to combine materials into ordered composite architectures. On the molecular scale, 'solvent templating' is used to control pore size in the range 0.3 – 0.7-nm needed for applications such as molecular sieving membranes. On the mesoscale, evaporation-induced self-assembly of surfactant/silica mesophases is used to prepare continuous, mesoporous films. By using micelles to spatially partition and organize organic precursors (within the hydrophobic micellar interiors) *and* inorganic precursors (surrounding the hydrophilic micellar exteriors) further self-assembly into liquid crystalline mesophases allows simultaneous organization of organic and inorganic precursors into various nanocomposite constructions. The evaporation-induced self-assembly approach can be extended to form nanostructured particles during aerosol processing and can be generalized to other composite architectures and other materials combinations (e.g. metal/oxide). Through co-organization of photosensitive molecules or polymers within ordered mesophases, we can achieve optically-mediated changes in mesostructural order, providing the first evidence of nanostructural lithography.

008. THE BIOGENESIS AND COOPERATIVE ASSEMBLY OF COMPLEX MATERIALS.

Galen D. Stucky, Daniel E. Morse, Paul K. Hansma, Bradley F. Chmelka, Timothy J. Deming and Mark Brzezinski, Departments of Chemistry, Materials, Molecular Biology, Physics, Chemical Engineering, and Marine Biology; University of California, Santa Barbara CA 93106

The biogenesis of materials evolves in a single system through a fascinating combination of the space/time definition of structure, function, and morphology at multiple length scales from complex mixtures of reactants and accessible processes. The assembly processes for these complex materials are carried out in a single system to give highly processed function and shape at all length scales even when high inorganic lattice energies are involved, as in the crystalline calcium carbonate-based abalone and sponge systems. Particularly interesting in the biogenesis of silicates is the creation of beautifully patterned structures on the meso and macro length scales starting with reactants in a near neutral pH environment at temperatures as low as -4 °C. Paradoxically, spatial and kinetic incompatibilities during the assembly of nanostructured organic/inorganic composite phases results in local instabilities that make it easy to temporally modify product composition, assembly, and macroscale form. Competing interactions and assembly processes generally have different entropic and kinetic handles that can be used to orchestrate hierarchical structure and functionality in the composite product. The relationships between *in vivo* and *in vitro* composite materials assembly and properties will be presented.

009.

SOLID STATE NMR CHARACTERIZATION OF SOL-GEL DERIVED ORGANICALLY MODIFIED SILICATES

Florence Babonneau , Chimie de la Matière Condensée, UPMC-CNRS, 4 place Jussieu, 75005 Paris, France.

Sol-gel processing of organically modified silicates is an area of rapid growth due to the wide variety of potential applications offered by these systems. They are prepared from organoalkoxysilanes RxSi(OR')4-x (x =1,2) and tetraalkoxysilane Si(OR")4, whose differences in reactivity towards hydrolysis and condensation reactions strongly influence the process of network formation. Structural characterization of the hybrid network is thus a key issue in the development of products, with optimized properties. This paper will present a review of solid state NMR techniques that can be used to probe the spatial proximity of different Si units in the hybrid netork : emphasis will be put on 2D 1H-29Si CP-MAS heteronuclear NMR correlations, and 17O MAS-NMR experiments.

010. RELEVANCE OF PHYSICAL CHEMISTRY TO DEVELOPMENT OF SOL-GEL DERIVED PRODUCTS.

J. D. Mackenzie, Eric Bescher, Department of Materials Science, University of California, Los Angeles, CA 90024

The sol-gel process for oxides can be divided into three separate but intimately related processes : 1. Complex reactions in the liquid state leading to the formation of porous wet gels ; 2. Drying of the wet gels at temperatures generally less than 200 C ; 3. Heat treatment of the dried gels to temperatures up to 1,000 C. The successful development of many useful sol-gel derived products is dependent on the understanding of the physical chemistry in all of the three processes mentioned. Currently there are insufficient physical-chemico results. Examples of the development of some specific sol-gel derived products in which there are important needs of physical chemictry research will be presented.

028.

HIERARCHICALLY ORDERED INORGANIC-ORGANIC COMPOSITES AND POROUS OXIDES, B. F. Chmelka, S.C. Christiansen, M.D. Mann, N.A. Melosh, P. Schmidt-Winkel, P. Yang, D. Zhao, and G.D. Stucky, Departments of Chemical Engineering and Chemistry; University of California; Santa Barbara, CA 93106

Sol-gel syntheses conducted in the presence of structure-directing surfactant agents or stabilized droplets allows inorganic-organic composites to be prepared over a wide range of tunable compositions and ordering length scales. In these systems, hydrolysis and polymerization of inorganic species tend to occur in hydrophilic regions of a sample, which are meso- or macroscopically phase-separated from hydrophobic regions. Ordering length scales and periodicities are typically established by the dimensions and arrangements of the hydrophobic aggregates, according to liquid crystal or block-copolymer self-assembly physics or on the packing of droplets in stabilized emulsions or micro-emulsions. Using such structure-directing agents in combination, it is furthermore possible to produce composite solids that are organized over multiple discrete and separately adjustable length scales. Recent results will be presented on molecular NMR investigations of inorganic-organic interfaces in these materials, from which physicochemical insights useful for selecting material processing conditions are obtained.

029.

SOL-GEL POLYMERIZATION OF ORGANOTRIALKOXYSILANES. EFFECT OF THE ORGANIC SUBSTITUENT ON GELATION. **Douglas A. Loy,** Brigitta M. Baugher, Duane A. Schneider, Sandia National Laboratories, Albuquerque, NM, 87185-1407

Silsesquioxanes, [RSiO1.5]n, are a family of siloxane network polymers that have become important as vechicles for introducing organic functionalities into sol-gel materials. However, there has not been a systematic study of the ability of organotrialkoxysilanes to form gels through the sol-gel process. In this study, we have examined the sol-gel chemistry off a variety of organotrialkoxysilanes (RSi(OR')3) with different organic groups (R = H, Me, Et, Pr, i-Pr, n-Bu, i-Bu, t-Bu, hexyl, octyl, decyl, dodecyl, hexadecyl, ocatdecyl, cyclohexyl, vinyl, phenyl, benzyl, phenethyl, chloromethyl, cyanoethyl,chloromethylphenyl, aminopropyl) with methoxide or ethoxide substitutents on silicon, at varying monomer concentrations, and with catalysts. Gels obtained from these polymerizations were processed as xerogels and characterized by solid state NMR, microscopy. and nitrogen sorption porosimetry.

030. SOL-GEL PROCESS IN 2-DIMENSIONS. R. M. Leblanc, S. Vidon, and S. Wang, Department of Chemistry, University of Miami, Coral Gables, Florida 33124

Polymerization process at interfaces has been a subject of considerable interest in the recent past. We investigated the chemical and photochemical induced polymerization phenomena at air-water interface and the polymerized Langmuir-Blodgett films were characterized by, microscopic and spectroscopic techniques. We studied the behavior of octadecyltrimethoxysilane (C_{18}TMS) at the air-water interface at different pH of subphase. C_{18}TMS monomolecular has been assigned to the one observed at pH around 5.0. Hydrolysis followed by condensation was observed when the pH was raised above 10.5 and lower than 3.0.

In another experiment we studied the dual polymerization (chemi- and photo-) at the air-water interface, for the first time, using ternary mixture of a C_{18}TMS, 10, 12-pentacosadiynoic (PDA) and *p*-10, 12-pentacosadiyne-1-*n*-tetraethyleneamide-α-*d*-manopyranoside (PDTM). Different dual polymerization behaviors of the mixed monolayers of PDA/PDTM/C_{18}TMS (7:1:8 molar ratio) at different subphase pH were noticed by recording surface pressure-area isotherms, Brewster angle microscopy images and UV-Vis spectra. The PDA/PDTM was isolated to small domains by C_{18}TMS linear polymer network and can only be polymerized weakly upon UV irradiation at pH 1.0. At pH 4.0, the partially hydrolyzed C_{18}TMS was miscible with PDA/PDTM and slowed the polymerization process of PDA/PDTM upon UV-irradiation. Applications of 2-D polymer process in the fabrication of chemi- and biosensors will be discussed.

031.

SURFACE AREA, POROSITY AND PYROLYSIS OF INORGANIC/ORGANIC HYBRID GELS DERIVED FROM POLYCARBOSILANES. **L.V. Interrante** Q. Liu, G. Soraru@, Chemistry Department, Rensselaer Polytechnic Institute, Troy, NY 12180-3590; @Università di Trento, Dipartimento di Ingegneria dei Materiali, Via Mesiano 77, 38100, Trento, Italy

Both hyperbranched and linear polycarbosilanes having the "average" formula "[Si(OR)2CH2]n" were used to prepare hybrid organic/inorganic gels by sol-gel processing. The structure of these gels and their pyrolysis to SiOxCy ceramics was studied by SS NMR and other methods, yielding detailed information regarding the precursor-to-ceramic conversion process. 29Si, 13C and 1H SS NMR and IR spectra show that the initial gels obtained from both "[Si(OR)2CH2]n" precursors after drying have a complex structure involving siloxy linkages and pendant Si-OR (R = H, Me or Et) groups in addition to the initial Si-CH2-Si bonding in the starting carbosilanes. After heating to 600 C, the gels become nearly fully condensed with an approximate "[Si(O)CH2]n" average formula. These gels were found to have relatively high surface areas (700-900 m2/g) and a microporous

032. ORGANIC/INORGANIC MOLECULAR HYBRID MATERIALS BY REVERSE SOL-GEL PROCESSING. R.M. Laine, L. Viculis, M. Z. Asuncion, H. Cheng, and R. Narayanan, Departments of Materials Science and Engineering, Chemistry, and the Macromolecular Science and Engineering Center, University of Michigan, Ann Arbor, Michigan 48109-2136

We have developed methods of synthesizing aluminum and silicon containing compounds directly from $Al(OH)_3$ and SiO_2. These compounds can be used to make numerous organic/inorganic hybrid materials including molecular hybrids with diverse properties including high porosity, high strength epoxy resins with flame resistance, and materials with olefinic linkages that exhibit high temperature stability.

049. STABILIZATION OF OXIDASES IN SILICA XEROGELS, Q. Chen, A. Heller*, J. Heller and G. Kenausis, Dept. of Chemical Engineering, Mail Code C0400, The University of Texas at Austin, Austin, TX 78712-1062.

A greater than 100-fold increase in the operational half-life of three enzymes - - glucose oxidase, lactate oxidase and glycolate oxidase - - was observed at 63° C upon their immobilization in hydrated silica gels formed by the sol-gel method. While glucose oxidase was massively stabilized, lactate oxidase and glycolate oxidase lost their activity. However, when lactate oxidase and glycolate oxidase were pre-complexed with a polycation that was more basic than the enzyme, a greater than 100-fold increase in half-life was again observed upon immobilization. The differences are explained by the structures of the enzymes. The entrance channels to the reaction zones in the α-hydroxy acid oxidases have positively charged arginine residues, attracting or guiding their substrate anions. Their electrostatic interaction with the anionic sites of the silica gel causes deactivation of the enzymes. When pre-complexed with and shielded by polycations, the polycations, not the arginine sites of the enzyme, interact with the anionic silica sites and encagement in silica stabilizes the enzymes.

050. PROBING THE BEHAVIOR OF BIOMOLECULES SEQUESTERED WITHIN SOL-GEL-DERIVED GLASSES. Frank V. Bright, Gary A. Baker, Meagan A. Doody, Siddharth Pandey, Neil J. Bonzagni and Cynthia M. Crago, Department of Chemistry, Natural Sciences Complex, State University of New York at Buffalo, Buffalo, NY 14260-3000

It is now widely accepted that sol-gel processing offers a relative facile means to entrap biorecognition elements within a porous glass matrix. Our research group has set its sights on better understanding the dynamics, thermodynamics, and photophysics of biomolecules when they are sequestered within these sol-gel-derived glasses and then using these insights to develop improved biosensors and biosensor arrays. This presentation will focus on our most recent efforts to elucidate the conformational changes and dynamics associated with the Ca^{2+}-dependent activation of spinach calmodulin (CaM) when this protein is dissolved in aqueous buffer or within binary mixtures of aqueous buffer and alcohol, and when CaM is actually sequestered within sol-gel-derived xerogel glasses.

051.

INTERACTIONS OF BIOLOGICAL MOLECULES WITH SOL-GEL GLASSES. **Bakul C. Dave** Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, IL 62901

Porous silica glasses obtained by the sol-gel route represent a unique matrix for encapsulation of biomolecules wherein the pores act as noncovalently interacting enclosures. The optically transparent nature of sol-gel matrices enables optical techniques to be used to study the properties of biomolecules encapsulated within the sol-gel matrix. This presentation will focus on interaction of biological molecules with different sol-gel matrices. Specifically, the following issues will be addressed: 1) effects of sol-gel encapsulation on stability and reactivity of encapsulated proteins and enzymes, 2) effects of encapsulation on photoinduced electron transfer reactions, 3) interactions of biological molecules with organically-modified silica sol-gels, and 4) interactions of biological molecules with nonmetal-doped silica sol-gels.

052.

IMMUNOASSAYS FOR DETECTION OF TRINITROTOLUENE USING SOL-GEL SILICA GLASSES. **E. H. Lan** B. Dunn, J. I. Zink, University of California at Los Angeles, Los Angeles, California 90095

Research in recent years has demonstrated that biological molecules such as enzymes, immunoglobulins, and other proteins can be immobilized in sol-gel derived matrices and retain their biological function. Development of glasses with encapsulated biomolecules has opened the possibility of solid-state optical biosensors for the detection and measurement of desired analytes. In this work, we report the successful use of sol-gel silica glasses with encapsulated antibodies for the detection of trinitrotoluene (TNT). Results show that both competitive immunoassay and displacement immunoassay are feasible using antibody-doped glasses. The optical transparency in silica glasses allows optical sensing using fluorescence. Calibration curves are derived correlating the fluorescence as a function of TNT concentration.

053. ACTIVATION PARAMETERS OF A XEROGEL ENCAPSULATED ENZYME/SUBSTRATE SYSTEM IMMERSED IN SUPERCRITICAL CARBON DIOXIDE. Brian C. Dunn, Thomas A. Cutler, Christopher R. Lloyd and Edward M. Eyring, Department of Chemistry, University of Utah, Salt Lake City, UT 84112 and NCDMF, Utah State University, Logan, UT 84322

In the presence of the enzyme cholesterol oxidase, cholesterol is oxidized by molecular oxygen to form cholesterone and hydrogen peroxide. Progress of the reaction can be monitored by oxidation of a dye, ABTS, that reacts with the H_2O_2 when peroxidase enzymes are present. Advantages of running this reaction with the enzyme encapsulated in a xerogel and immersed in supercritical carbon dioxide ($scCO_2$) are that cholesterol and cholesterone are more soluble in this solvent than in an aqueous medium and xerogel encapsulation protects the enzyme from denaturation by this warm ($t > 42°C$), high pressure ($P > 100$ bar) solvent. Spectroscopic measurements of reaction rates over a range of temperatures and pressures yield activation parameters from which mechanistic inferences can be drawn. The mechanism of the cholesterol oxidase catalyzed reaction in an aqueous medium is compared to that in $scCO_2$.

054.

DYNAMICS AND REACTIVITY IN SOL-GEL ENCAPSULATED PROTEINS. **Joel M. Friedman** T. K. Das, D. S. Gottfried, L. J. Juszczak, I. Khan, E. S. Peterson, D. L. Rousseau, C. Shannon, U. Samuni, Dept. of Physiology/Biophysics, Albert Einstein College of Medicine, Bronx, NY 10461.

We are addressing the question of how encapsulation alters functionally-important protein dynamics. Myoglobin, hemoglobin and transferrin were chosen for study since, respectively, they exhibit dynamics arising from progressively larger amplitude motions. The conformations and conformational dynamics of the encapsulated proteins were monitored through a combination of cw and time-resolved optical spectroscopies including UV and visible resonance Raman, fluorescence and absorption. Reactivity of the encapsulated proteins was followed through ligand binding kinetics (geminate and bimolecular recombination for the hemeproteins and iron uptake and release for transferrin). The results show that small amplitude motions are not significantly altered, but large amplitude motions such as quaternary structure changes are greatly impeded allowing for the trapping of nonequilibrium species.

055. SPECIAL EFFECTS OF GLASS MATRICES ON PROTEIN CONFORMATION, UPTAKE EQUILIBRIUM, AND CATALYTIC ACTIVITY

Jovica Badjić, Ekaterina N. Kadnikova, and Nenad M. Kostić
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Because of steric and electrostatic properties of sol-gel glasses made of silica and alkylated silica, encapsulated proteins and small molecules behave differently in glass matrices and in solutions. Unique properties of glasses affect electrostatic interactions of proteins and small molecules (e. g., enzymes and their substrates), stability of proteins toward unfolding, catalytic activity of peroxidases and esterases and transfer of small molecules between the glass matrix and external solution. These special effects should be considered in the design of biosensors, heterogeneous catalysts and other composite biomaterials. We will report kinetic studies of electron-transfer reactions and of catalytic oxidations and hydrolyses and will show that hydrogen bonding greatly affects uptake and release of guest molecules by glass matrices.

072.

RECENT ADVANCES IN THE ELECTROCHEMISTRY OF SOL-GEL DERIVED SILICATES AND ORGANICALLY MODIFIED SILICATE ELECTRODES. O. Lev, S. Bharathi, S. Sampath, J. Gun, L. Rabinovich , Fredy and Nadine Herrmann Graduate School of Applied Science, The Hebrew University of Jerusalem, Jerusalem 91904, Israel

Increasing attention has been devoted during recent years to sol-gel modified electrodes and their possible applications in electrochemical and biochemical sensing. Recent advances in this field will be reviewed with an emphasize on developments that were originated in our laboratory. Several classes of composite modified electrodes including composite carbon - Ormosil electrodes and noble metal nanoparticles - organically modified silicate composite electrodes will be presented and discussed.

073. MATRIX EFFECTS ON ELECTROCHEMICAL REACTIONS IN SOL-GEL MATERIALS. James A. Cox, Department of Chemistry and Biochemistry, Miami University, Oxford, Ohio 45056

Sol-gel materials are being evaluated as electrolytes for electrochemistry in the absence of a contacting liquid phase. The voltammetry of hosted materials is subject to perturbation by the pore structure and by ion-exchange reactions with the backbone material. The effective diffusion coefficient, D_{eff}, of selected monomeric dopants in silica is dependent on apparent pore diameter. With polyoxometalates, D_{eff} varies over the range 10^{-8} to 10^{-6} cm^2s^{-1} as the silica is templated to change from a microporous to mesoporous material. With polymeric dopants such as Prussian Blue, the values remain in the range 10^{-8} cm^2s^{-1}.These data reflect the relative contributions of physical diffusion and electron self-exchange to D_{eff}. A role of ion-exchange on redox pathways in silica will be shown by measurement of the rate of disproportionation of UO_2^+. How these results allow optimizing doped gels as platforms for sensors and as electrocatalysts for redox of gaseous species will be discussed.

074.

THE PHYSICAL AND CHEMICAL PROPERTIES OF SILICA AEROGELS PAVED WITH NANOWIRES. **Debra R. Rolison,** J.V. Ryan, C.I. Merzbacher, J.W. Long, M.L. Anderson, A.D. Berry, and R.M. Stroud, Naval Research Laboratory, Washington, DC 20375

Aerogels are nanoscale mesoporous materials in which high surface area domains are networked in a volume that is >85% open space thereby providing rapid molecular flux into the structure. Nanoscale ruthenium dioxide has been deposited onto the inner and boundary surfaces of densified silica aerogels using a low temperature synthetic protocol in which molecular precursors can be pre-adsorbed onto the surface of densified silica aerogels and decomposed without raising the temperature above 273K. A single adsorption/decomposition cycle creates a 50-75% weight gain and yields an electronically conductive aerogel in which ~2-nm deposits of ruthenium dioxide define percolation paths over >50 sq-m of aerogel surface. Impedance spectroscopy, thermal and x-ray analyses, microprobe Raman spectroscopy, transport measurements, and transmission electron microscopy are used to characterize the aerogel-supported nanowires.

075.

A NEW TEMPLATE APPROACH TO PRODUCTION OF ULTRA-HIGH SURFACE AREA LITHIUM ION INTERCALATION MATERIALS. **Daniel A. Buttry** Eiichi Shoji, University of Wyoming, Dept. of Chem., Laramie, WY, 82071-3838

A new method for producing ultra-high surface area inorganic oxides will be described. The method is based on use of polymeric templates which serve to direct the growth of the inorganic oxide matrix from a typical sol-gel solution. We will describe two systems, one using a conducting polymer precursor as template, and another using a novel redox polymerizable organosulfur compound. We will describe the electrochemical characteristics of these matrials, as well as their characterization with SEM-EDS, ellipsometry, X-ray diffraction, infrared, Raman and UV-Vis spectroscopy.

093.

MOLECULES AND CHARGES AT THE AQUEOUS INTERFACE OF MICROSCOPIC PARTICLES: POLYMER BEADS, EMULSIONS, SEMICONDUCTORS, AND LIPOSOMES. **Kenneth B. Eisenthal** Y Liu, E. Yan, D. Zimdars, J. Dadap, A. Srivistava, X. Zhao, S. Ong, H. Wang, Department of Chemistry, Columbia University, New York 10027

Second harmonic gerneration studies of the electrostatic and acid-base properties of the silica/ aqueous interface will be presented. A recent breakthrough that has enabled us to selectively probe the molecules absorbed and the effect of charges at the liquid interface of microscopic particles will be presented. Results on the following microscopic particles will be discussed: polymer beads, oildroplet/ water emulsions, spectra of TiO_2semiconductor microparticle charge transfer complex, and the absorption to the liposome/ aqueous interface and the dynamics of molecular transport across the liposome bilayer.

094. OPTICAL EXCITATION AND DYNAMICS IN SOL-GEL DERIVED NANOSTRUCTURED MATERIALS. P. N. Prasad, A. Biswas, C. Friend, J. Swiatkiewicz, M. Lal, and G. Manchala, Photonics Research Laboratory, Department of Chemistry, 428 NSM Complex, State University of New York at Buffalo, Buffalo, New York 14260-3000

Sol-gel processing provides opportunities to make nanoparticles and multiphasic nanocomposites for the exciting new field of nanophotonics. Also, photonic processes can be used to probe interaction and dynamics in a sol-gel medium. In this talk, we present our sol-gel approach to make nanoparticles, nanomers and nanocomposites. Optical excitation and dynamics in these media have been investigated using linear and nonlinear optical techniques and time-resolved pump-probe methods.

095.

STABILIZATION OF RU(II) POLYPYRIDYL COMPOUNDS IN MESOPOROUS SOL-GEL PROCESSED TITANIUM DIOXIDE FILMS. Ping Qu, Craig A. Kelly, David Thompson, Fereshteh Farzad, and Gerald J. Meyer, Department of Chemistry, Johns Hopkins University, Baltimore, MD 21218.

We have recently found that photo-unstable Ru(II) polypyridyl compounds are stabilized when anchored to sol-gel processed colloidal TiO_2 (anatase) films. Temperature dependent photophysical studies demonstrate that the activation energy for metal-to-ligand charge transfer (MLCT) → ligand field state, internal conversion increases dramatically when the complexes are anchored to the semiconductor surface. Therefore, Ru(II) complexes that are photochemically unstable and non-luminescent in fluid solution display efficient luminescence and long-lived excited states when surface bound. Interestingly, the quantum yield for interfacial electron transfer from the MLCT excited states into the TiO_2 particles can be tuned by varying the concentration and identity of cations exposed to the film. A model where the acceptor states in TiO_2 shift with cation adsorption will be presented.

096.

METAL ACTIVATOR-FREE SILICATE PHOSPHORS

Michael J. Sailor, Will H. Green and Michael A. Ansell; Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, 0358, La Jolla, CA 92093

The sol-gel reaction of tetramethoxysilane (TMOS) or tetraethoxysilane (TEOS) with a variety of carboxylic acids leads to a solid glass within a few minutes to a few days. The as-prepared silicate glasses show no photoluminescence (PL) but a simple heat treatment in air between 200 deg C and 500 deg C produces a material that displays white PL between 450-600nm. The external PL quantum yield, measured under 365-nm excitation, ranges from 0.20 to 0.45 and the PL lifetime is < 10 ns. The chromophore is proposed to be a silicate-traped polyaromatic species. A second class of luminescent materials was synthesized by the reaction of various carboxylic acids with amino-functional trialkoxysilanes such as 3-aminopropyltriethoxysilane (APTES). The transparent yellow-orange polysiloxane that forms from the reaction of formic acid and APTES is highly luminescent (F=0.3-0.4) and is water soluble. The chromophore in 3-aminopropylsiloxanes is proposed to be a cyclic silyl imidate species. Model compound studies and molecular orbital calculations aimed at obtaining a better understanding of the nature of the chromophore in these materials will be discussed.

097.

LONG-LIVED LUMINESCENT DEFECT SITES IN PURE SILCA XEROGELS. **A. E. STIEGMAN**, A. S. Soult, Department of Chemistry, Florida State University, Tallahassee, Florida, 32306

Silica xerogels, made from the hydrolysis and condensation of silicon alkoxides, possess luminescenct sites that are inherent to the xerogel. At room temperature, a single emission is observed at 353 nm. The emission is very long lived with a lifetime of (0.85 sec) and is also vibrationally structured. At cryogenic temperatures (77 K), a second long-lived emission appears at 420 nm with a lifetime of 0.93 sec. Both of these species show significant quenching by oxygen. The intensity of the luminescent site emission varys with processing temperature of the xerogel and, upon calcining (900° C), they disappear altogether. Franck-Condon analysis of the vibrational progression observed in the emission are compared to vibrational modes observed in Raman spectra of the materials which suggests specific structural features, unique to the sol-gel derived silica, that give rise to the emission. Photochemical properties of these luminescent sites will also be discussed.

098. SYNTHESIS AND CHARACTERIZATION OF SILICA AEROGEL MONOLITHS BULK-MODIFIED WITH COVALENTLY BOUND 2,7-DIAZAPYRENIUM MOIETIES. N. Leventis*, I. Elder, D. Rolison*, and C. Merzbacher, Department of Chemistry, The University of Missouri at Rolla, Rolla, MO 65409, Surface Chemistry Branch (Code 6170) and Optical Physics Branch (Code 5610) Naval Research Laboratory, Washington, DC 20375.

Silica aerogels were covalently modified with *N*-(3-trimethoxysilylpropyl)-2,7-diazapyrenium bromide (DAP). No leaching of DAP occurred during either washing or supercritical drying of the organomodified gels. The bulk concentration of the dye in the aerogels was ≤7.0 mM, and the surface coverage < 0.04 ML. The samples demonstrate bulk photoluminescence. The bulk density (0.17 g/cm^3), N_2-adsorption surface area (~870 m^2/g) and TGA characteristics of the dye-modified aerogels are identical to those of unmodified aerogels. The adsorption, and emission of DAP in the aerogel parallel those in alcoholic solution indicating that the DAP moieties are isolated from each other in an environment with -OH polarity. Time-resolved emission indicates that DAP is located in two types of microenvironment. O_2 emission quenching of *ca.* 1-cm diam. aerogel monoliths is complete in 15 s, competing very favorably with μm-thick xerogel films. The apparent diffusion coefficient of O_2 or Ar in the aerogel monoliths was estimated to be 0.01-0.02 cm^2/s, which is only 10x less than the unimpeded diffusion coefficient of Ar in air.

099. PHOTOCONUCTIVITY IN SiO2 SOL-GEL SAMPLES DOPED WITH LASER DYES. J. Garcia M, Instituto de Física, UNAM, P.O. Box 20-364, 01000 México, D.F.

Sol-gel glasses doped with laser dyes have good potential for non-linear optical applications like phase conjugation, harmonic generation and holographic recording. These processes are somehow dependent on the charge transport produced inside the sample when it is illuminated and subjected to an applied electric field. We have studied photoconductivity on SiO2:RhB sol-gel samples. The J(E) response curves show three regions. A linear one corresponding to the ohmic behavior. Then a non-linear region in which a maximum is observed, due to the polarizability of the dye molecules. And finally another region where a continuos decay is observed, reaching an asymptotic limit independent of the illumination wavelength. These results are discussed and the calculated charge transport parameters are given.

122.
THE STRUCTURE AND DYNAMICS OF SOL-GEL GLASSES BY TIME-RESOLVED OPTICAL, SPECTRAL HOLE-BURNING, GAS ADSORPTION ISOTHERM, AND NEUTRON DIFFRACTION STUDIES. **Eric L. Chronister,** Patrick Lloyd, Department of Chemistry, UC Riverside, Riverside. CA 92521

The porous microstructure of silica and aluminosilica xerogel glasses is investigated with both small angle and quasi-elastic neutron scattering as well as gas adsorption isotherm measurements. These results are used to obtain the dimensions and distributions of xerogel pore sizes and to correlate them with sol-gel chemistry and photophysics. Time-resolved fluorescence anisotropy measurements are used to reveal the changes in rotational diffusion associated with the sol to gel to glass transitions. Changes in the local viscosity and/or volume of the rotating unit is used to probe the association of dopants with the sol-gel matrix. Time resolved absorption and emission studies of sensor chromophores doped into xerogels are used to characterize diffusion of analyte molecules through porous matrices. Finally, temperature

123.
ORIENTATIONAL DYNAMICS OF LIQUIDS CONFINED IN NANOPOROUS SOL-GEL GLASSES. **John T. Fourkas** Brian J. Loughnane, Richard A. Farrer, and Alessandra Scodinu, Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, MA 02467

Optical Kerr effect (OKE) spectroscopy has been used to measure the orientational correlation function of wetting and nonwetting liquids confined in nanoporous silicate sol-gel glasses. The OKE technique allows us to extract quantitative microscopic information about liquids in these systems, including the rate of surface reorientation, the thickness of the surface layer of the liquid, and the rate of exchange of molecules of wetting liquids off of the glass surface.

124.
DYNAMIC STRUCTURE OF LIQUIDS IN NANOPOROUS GLASSES. **Jiri Jonas,** Beckman Institute for Advanced Science and Technology, University of Illinois at Urbana-Champaign, Urbana, IL 61801

An overview of systematic experimental and theoretical NMR studies of the dynamics of molecular liquids confined to porous silica sol-gel glasses with pore radii in the range from 10Å to 100Å is presented. The main topics discussed are as follows: 1) The relative role of surface and topological effects on nuclear relaxation rates of polar and non-polar molecular liquids; 2) High-resolution NMR of confined liquids; 3) The effect of confinement on anisotropic rotational diffusion; 4) Quenched molecular reorientation and angular momentum for confined liquids; and 5) The pressure effects on dynamics of confined liquids. The molecular liquids investigated ranged from non-polar liquids such as methylcyclohexane and carbon disulfide to polar liquids of acetonitrile, pyridine, nitrobenzene, and 2-ethylhexyl benzoate.

125. MAGNETIC RELAXATION DISPERSION STUDIES OF LIQUIDS IN CONFINED ENVIRONMENTS. J.-P. Korb, R. G. Bryant, Laboratorie de Physique de la Matère Condensée, CNRS, Ecole Polytechnique, Palaiseau, France, Chemistry Department,University of Virginia, Charlottesville, VA, USA.

The magnetic field dependence of the nuclear spin-lattice relaxation rate provides a map of the Fourier transform of the correlation functions that create the magnetic noise which drives magnetic relaxation. In liquids, the correlation times are generally very short, but in the case where electron spin interactions contribute significantly to relaxation, high frequency dynamics may be extracted from the nuclear resonance experiments. In high surface area systems often associated with liquid confinement, the spin-relaxation dispersion reports low frequency events that may, nevertheless, be understood in the context of rapid molecule motion but where the confinement constrains the space explored by the diffusing spin during the relaxation process. Analysis of several high surface systems demonstrates important correlations between the relaxation dispersion and surface roughness, molecular size, and surface loading of paramagnetic relaxation sinks. Liquids studied include water, DMSO, acetonitrile, acetone, and dimethyl formamide on microporous glasses and synthetic silicate materials of controlled dimensionality.

126.
STRUCTURAL CHARACTERIZATION OF POROUS NANOPHASE MATERIALS BY CONTRAST-MATCHING SANS. **Celia I. Merzbacher,** D. R. Rolison, M. L. Anderson, V. M. Cepak, K. E. Swider, Naval Research Laboratory, Washington, DC 20375; J. G. Barker, NIST, Gaithersburg, MD 20899

Contrast-matching small-angle neutron scattering (SANS) is a powerful tool for structural characterization of porous materials with two solid phases on the scale of 1-100 nm. By filling the pores with a liquid having neutron scattering properties that match one phase, scattering will result solely from the second phase. Due to the large difference in scattering length of hydrogen and deuterium, mixtures of H2O and D2O can be used to match many phases. This technique has been particularly helpful in the study of two-phase aerogels, including Ru-Ti oxide aerogels condensed from a mixed-metal sol and various aerogel composites formed by deposition of a second phase on the internal surfaces of silica aerogel. The scattered intensity as a function of wavevector reveals smooth vs. rough (or fractal) structures and morphologies on the nanoscale.

127.

PHASE STABILITY IN PERIODIC SILICA/SURFACTANT NANOSTRUCTURED MATERIALS.

Sarah H. Tolbert, Junjun Wu, Adam Gross, Xiaoyang Liu, and E. Janette Ruiz, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA, 90095-1569

The study of phase transitions can be used to learn about the factors controlling stability in complex nanostructured materials. Low angle X-ray diffraction is utilized to follow phase behavior in ordered silica/surfactant composites in real time. Experiments performed under hydrothermal conditions allow us to correlate framework structure and synthesis conditions with hydrothermal stability. Temperature-induced changes in surfactant packing drive overall changes in periodicity; framework structure and synthesis conditions, however, control the kinetics of the reaction. Under externally applied hydrostatic pressure, extremely high stability is observed. Despite a nanostructure with silica walls less than 15 angstroms thick, the compressibility of these composites is almost identical to bulk amorphous silica. This fact likely stems from the nearly ideal nanoscale architecture of the inorganic framework.

APPENDIX III

SYMPOSIUM ABSTRACTS

POSTER SESSION

PHYSICAL CHEMISTRY OF SOL-GEL MATERIALS

207.
RAMAN STUDY OF LIQUID METHYL IODIDE CONFINED IN POROUS SILICA XEROGEL MONOLITHS: AUTOREGRESSIVE BAND SHAPE ANALYSIS. **E. L. Quitevis,** R. E. Wilde, and T. R. Bryans, Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, TX, 79409

The spontaneous Raman spectra of the v2 and v3 bands of liquid methyl iodide confined in 60-Å diameter pores of silica xerogel monoliths were measured at room temperature. The xerogels were made by using an adaptation of the fast sol-gel method. The band shapes for the confined liquid are broader than for the neat liquid. For the v3 band, the broadening is particularly noticeable in the wings of the depolarized spectrum. The autocorrelation functions were obtained by Fourier transforming the isotropic and depolarized band profiles. The vibrational-correlation and memory functions were analyzed by a memory-function modelling procedure and by an autoregressive time-series analysis. The analysis allowed the separation of the homogeneous and inhomogeneous second moments.

208.
TEMPERATURE - DEPENDENT ROTATIONAL DYNAMICS OF CARBON DISULFIDE CONFINED IN NANOPOROUS GLASSES. **Brian J. Loughnane** and John T. Fourkas, Eugene F. Merkert Chemistry Center, Boston College, Chestnut Hill, MA, 02467

The orientational dynamics of carbon disulfide confined within nanoporous glasses are investigated using Optical Kerr effect spectroscopy. Our results sugest that the rotational dynamics of molecules near the surface are much slower than previously believed. Suface relaxation at room temperature in small pores is more than an order of magnitude slower than the bulk relaxation at the same temperature. We demonstrate a clear relationship between the size of the pore and the rate of surface relaxation, which suggests that the slower dynamics primarily arise from geometrical effects.

209.

EFFECTS OF THE REACTION MEDIUM ON OXIDATION OF ORGANIC SUBSTRATES CATALYZED BY PEROXIDASES IN SOL-GEL GLASS

Ekaterina N. Kadnikova and Nenad M. Kostić
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Horseradish peroxidase encapsulated into silica glass monolith by the sol-gel method retains its spectroscopic properties and its ability to form Compound I upon treatment with hydrogen peroxide. Even though HRP in solution catalyzes chemoselective conversion of thioanisole to the corresponding sulfoxide, the encapsulated enzyme does not catalyze this reaction. Microperoxidase-11 is a better catalyst than HRP both in solution and in the glass. Both HRP and MP-11 efficiently catalyze one-electron oxidation of ABTS. In the organosilica glass conversion of ABTS to $ABTS^{+\bullet}$ does not depend on the identity of the alkyl groups or the ABTS concentration. In the silica glass conversion of ABTS increases as the ABTS concentration increases because of the differences in the hydrophobicity of the matrix.

210. UNFOLDING OF BOVINE CARBONIC ANHYDRASE II ENTRAPPED IN SOL-GEL GLASS

Jovica Badjić and Nenad M. Kostić
Department of Chemistry, Iowa State University, Ames, Iowa 50011

Bovine carbonic anhydrase II is encapsulated in the porous, transparent silica monolith glass prepared from TMOS. The enzyme doesn't leach from the glass and retains its overall conformation and esterase activity. Circular dichroism studies showed that the enzyme is only 80 % unfolded by heating or by addition of guanidine hydrochloride under conditions when the enzyme in solution is completely unfolded. Encapsulation prevents precipitation upon heating (which occurs in solution) and allows determination of the apparent melting point of 51 ± 3 °C. Steric constraint of the encapsulated enzymes by the glass matrix must be considered in design of sensors.

211.

MOLECULAR IMPRINTING IN GUANIDINE FUNCTIONALIZED SOL-GEL MATERIALS.

D.Y. Sasaki, T. M. Alam, R. A. Assink, B. Hart*, K. J. Shea* Sandia National Laboratories, Albuquerque, NM and *UC Irvine, Irvine, CA

Recognition sites for phosphonate substrates were prepared in silica sol-gel materials using a molecular imprinting technique. Guanidine- and ammonium-silanes were used as monomers to functionalize a silica xerogel surface while employing phenylphosphonic acid (PPA) as a template to generate the receptor sites. Affinity studies were conducted on the materials using batch and chromatography studies. In the presence of water, the guanidine functionalized imprinted materials exhibited much higher affinity for phenylphosphonic acid (PPA) than the ammonium functionalized materials indicating possible hydrogen bond interactions. 31P NMR solid state studies were used to evaluate the binding interactions at the functionalized surface.
Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.

212.

INFLUENCE OF SURFACE AREA ON THE ELECTROCHEMICAL PROPERTIES OF SOL-GEL DERIVED TRANSITION METAL OXIDES. **Winny Dong,** John H. Harreld and Bruce S. Dunn, UCLA, Materials Science and Engineering, 5704 Boelter Hall, Los Angeles, CA 90095

Abstract: The limiting reaction in a lithium intercalating cathode material is the diffusional process. Aerogels offer a solution to this problem because with its high surface area, surface reactions should dominate. By using transition metal oxide aerogel powders of varying surface areas with a sticky carbon electrode, the influence of surface area on the electrochemical properties can be determined. The aerogels were dried supercritically and ambiently with different solvents to achieve surface areas between 10 to 400 m^2/g. To further distinguish between surface reactions and diffusional intercalation, tetrabutylammonium perchlorate was used as a salt in place of lithium perchlorate. The size of the tetrabutylammonium perchlorate inhibits the ions from intercalating into the material, hence only surface reactions were observed with this salt.

213.

A SOL-GEL APPROACH TO RIGID WELL-DEFINED THIN FILMS. Jason H. Rouse, Barbara A. MacNeill, Gregory S. Ferguson. Departments of Chemistry and Materials Science and Engineering, Lehigh University, Bethlehem, Pennsylvania 18015-3172

Sol-gel processing of tetraethyl orthosilicate (TEOS) within a multilayer film, formed by the alternate absorption of poly(diallyldimethylammonium chloride), and a synthetic silicate sheet mineral, Laponite, results in an interpenetrating composite network of silicon dioxide within the multilayer. Kinetic data indicate that the rate of TEOS sorption and oligomerization reaches a steady-state value within a day. Curing the TEOS-treated films to complete the polymerization process results in a rigid film whose swellability upon changes in humidity is dramatically reduced compared to the original film.

214.

'SMART GLASSES: ENVIRONMENTAL SENSITIVITY OF A NOVEL ORGANICALLY-MODIFIED SILICA SOL-GEL. **Mukti S. Rao,** and Bakul C. Dave, Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, IL 62901-4409

The environmental sensitivity of a novel organically-modified silica sol-gel is reported. The environmentally-responsive behavior of these material is due to an incorporation of a specific response-active bis-(propyl)ethylenediamine organic spacer unit in the silica backbone. The material, when fabricated in the shape of a macro-tweezers can be made to open or close its arms reversibly with respect to changes in several external variables including temperature, ionic concentration, and electric potential. The response to the stimuli can be controlled by varying the composition of the material by a precise choice of precursors. Sol-gels with a greater hydrophilic character show enhanced response to environmental stimuli. These materials provide an initial example of 'molecular design' approach to generate programmed smart responses from sol-gel–derived silica.

216.
SOL-GEL SYNTHETIC ROUTES TO NOVEL LITHIUM ION INTERCALATION MATERIALS.
Kevin C. White Daniel A. Buttry, University of Wyoming, Dept. of Chem PO Box 3838, Laramie, WY, 82071-3838, Roberta Torresi, Susana Toressi de Cordoba, Instituto de Química de São Carlos - USP, CP 780 - 13564-970 São Carlos (SP)

Slow lithium cation intercalation into metal oxide cathodes represents a major kinetic limitation for their use in secondary battery systems. Our goal is the manipulation of these materials, through the inclusion of guest species, in order to understand how changes in morphology manifest themselves in the charge-discharge characteristics of the cathode material. Synthesis of vanadium pentoxide host materials through sol-gel techniques has proven to be a useful method to include a wide variety of guest species, including transition metal complexes and polymeric species. Recent progress with this approach will be discussed, including characterization with electrochemistry, ellipsometry, X-ray diffraction, infrared, raman and UV-Vis spectroscopy.

217.
SYNTHETIC CONTROL OVER THE FABRICATION OF HOMOGENEOUS VANADIA-SILICA XEROGELS. **A. E. Stiegman,** M. D. Curran, Department of Chemistry and the Materials Research and Technology Center (MARTECH), Florida State Univeristy, Tallahassee, FL 32306

Multicomponent vanadia-silica glasses have been synthesized from the co-condensation of oxovanadium triisopropoxide with tetramethylorthosilicate. It has been found that by control of specific variables of the multicomponent sol-gel process, phase separation into distinct V2O5 and SiO2 phases can be suppressed and amorphous, homogeneous xerogels can be produced with relatively high vanadium content. Parameters such as the vanadium concentration, water content, aging time, and pH, have been shown to affect the chemical species formed during the solution phase of the sol-gel process which, in turn, profoundly affect the homogeneity of the xerogels. Of these parameters, the use of an acid catalyst capable of both catalyzing the sol-gel reaction and reducing the vanadium from V(V) to V(IV) has been shown to have the most dramatic impact on the homogeneity of the final xerogel allowing loadings as high as 14.0 mol % V to be realized.

215.
DESIGN OF NOVEL SOLID STATE BIOCATALYSTS BY SOL-GEL ENCAPSULATION OF ENZYMES. **Robyn Obert,** and Bakul C. Dave, Department of Chemistry and Biochemistry, Southern Illinois University at Carbondale, IL 62901-4409

The encapsulation of proteins and enzymes in a sol-gel matrix offers the benefits of enhanced stability. This presentation will focus on use of sol-gel encapsulation of enzymes to design novel solid state biocatalysts. This presentation will focus on use of coupled enzyme system based on sol-gel encapsulated alcohol dehydrogenase, formate dehydrogenase, and formaldehyde dehydrogenase for novel catalytic applications. The sol-gel containing these enzymes functions as novel biocatalyst for conversion of isothermal conversion of carbon dioxide to methanol. The results provide evidence that sol-gel encapsulation can be used to develop stable and efficient biocatalysts.

218. SYNTHESIS AND ULTRAFAST ELECTRONIC RELAXATION DYNAMICS OF PbI_2 COLLOIDAL NANO-PARTICLES. J. Z. Zhang and A. Sengupta, Department of Chemistry, University of California, Santa Cruz, CA 95064

The first direct measurements of ultrafast electronic relaxation dynamics in PbI_2 colloidal nano-particles have been performed using femtosecond laser spectroscopy. The PbI_2 nano-particles were prepared using colloidal chemistry methods in different solvents and polymer matrix. The particle size was determined using transmission electron microscopy. The electronic absorption spectra show blue shift with decreasing particle size and suggest that the particles are in the quantum confined regime. With 390 nm excitation and probing in the near infrared, the electronic relaxation dynamics in PbI_2 nano-particles were monitored. The relaxation is found to be sensitive to solvent and insensitive to particle size. Early time oscillations were observed and the oscillating period changes with solvent but not with size. The oscillations are possibly quantum beats associated with surface states or phonons. The results suggest that the surface plays a major role in the electronic relaxation process of PbI_2 nano-particles.

219.
IMPEDED ROTATION OF A PROTEIN IN A SOL-GEL MATRIX. **David S. Gottfried,** Anna Kagan, and Joel M. Friedman, Dept. of Physiology and Biophysics, Albert Einstein College of Medicine, Bronx, NY 10461.

The functionality of proteins encapsulated within sol-gel matrices has been demonstrated, however little biophysical characterization of the proteins has been done. In this study, time-resolved fluorescence anisotropy was used to compare the rotational mobility of two probes in sol-gels derived from different preparative methods. A small molecule, sulforhodamine 101, was used to gauge the relative solvent viscosity within the sol-gels and reveals both low and high mobility encapsulation sites whose populations are dependent on gel preparation and age. Magnesium protoporphyrin IX-substituted myoglobin provides a convenient probe of global rotational dynamics of a typical globular protein and shows greatly-diminished decay of the fluorescence anisotropy in two of the three gels prepared. This is consistent with restrictive encapsulation sites whose size and/or environment substantially impedes rotational diffusion.

220. DYNAMICS OF CURVED DNA MOLECULES IN POLYACRYLAMIDE GEL. U. Mohanty,Department of Chemistry, Boston College, Chestnut Hill, MA 02167

A theory for gel retardation of intrinsically curved DNA (A-tracts) is described that takes into account in an approximate way the low and the high frequency visco-elastic response of the gel matrix, conformation of the "probe" chain, dihedral barriers and transverse friction drag forces. Dynamical motions of the "probe" chain are accompanied by viscoelastic response of the "vivinal" chains via reptation. In accord with experiments, analysis shows that the gel-mobility of DNA with a bend at the center is slower than that of the same molecule with a bend at its end. We have also obtained generalization of tube reptation model of gel-retardation of DNA that takes into account the observed orientational and dynamic nature of the agarose gel matrix.

221.
CONCENTRATION EFFECTS ON THE MORPHOLOGY OF CO-PRECIPITATED MIXED METAL OXALATES. **Karl F. Schoch, Jr.,** Carol J. Painter, Theodore R. Vasilow, Northrop Grumman Corporation, Electronic Sensors and Systems Sector, Science and Technology Center, 1350 Beulah Rd., Pittsburgh, PA 15235

Thermal decomposition of mixed metal oxalates is a well known process used to form ferrites. The concentration of reagents during precipitation of the mixed oxalate precursors is critical for controlling the morphology and particle size of the precipitates. This paper describes the effects of variation in concentration of acetic acid and oxalic acid. The particle size and morphology of the precipitate was affected by the reagent concentrations, but the composition of the product was not.

222.

DENDRIMER/SOL-GEL COMPOSITES: TOWARDS SOLUTION-PHASE CHEMICAL SENSING.

Peter J. Skrdla, S.Scott Saavedra, Richard M. Crooks, Neal R. Armstrong, Department of Chemistry, University of Arizona, Tucson, Arizona, 85721

Dendrimer technology is one of the most rapidly growing synthetic fields in macromolecular chemistry. Applications include nanoscale catalysts and reaction vessels, chemical sensors and separation media. We have begun to explore the physical and chemical properties of sol-gel/dendrimer composite materials. Globular fourth generation poly(amido-amine) (PAMAM) dendrimers have been encapsulated in sol-gel matrices to give novel 'three-phase' composites which have properties amenable to chemical sensing and separation science. Issues directly related to these fields that have been addressed include dendrimer leaching from sol-gel monoliths, partitioning behavior of organic analytes into these supramolecular organic/inorganic hybrid structures, as well as studies of dye loading and quenching effects. Finally, polarity sensitive indicators were used to probe the microenvironment inside these materials.

223.

COMPARATIVE STUDY OF ZNO NANOPARTICLES PREPARED BY SOL-GEL, REVERSE MICELLE AND LASER VAPORIZATION TECHNIQUES.

M. Samy El-Shall , S. Li and I. Germanenko, Department of Chemistry,
Virginia Commonwealth University, Richmond, VA 23284-2006

ZnO nanoparticles have been prepared by sol-gel, reverse micelle and laser vaporization techniques. All particles have the bulk crystal structure and show quantum size effects in absorption and emission. The particles produced by the sol-gel method are the smallest (4 nm diameter), but all show bandgap shifts and size-dependent dispersed and time-resolved emission spectra. They show emissions that consist of a blue bandgap feature with a sub-nanosecond lifetime and a green feature with multiexponential lifetime decays. Emission from the stearate coated particles produced by the reverse micelle method is particularly intense. The effect of water on the photoluminescence properties will be discussed.

224.

PHOTOLUMINESCENCE QUENCHING OF SILICON NANOCRYSTALS BY ELECTRON ACCEPTORS.

M. Samy El-Shall , S. Li and I. Germanenko, Department of Chemistry,
Virginia Commonwealth University, Richmond, VA 23284-2006

Weblike aggregates of coalesced Si nanocrystals are prepared by the Laser Vaporization Controlled Condensation (LVCC) technique. Upon excitations with visible or UV light, the Si nanocrystals show red photoluminescence whose multiexponential time decays are characterized by lifetimes that range from 20-80 microseconds, depending on the emission wavelength. The red emission can be quenched with electron acceptors whose redox levels lie below the conduction band edge of the Si nanocrystals. The quenching rate constants for 4-nitrobenzonitrile; 1,4-dinitrobenzene and 3,5-nitrobenzonitrile are obtained from Stern-Volmer plots. The results are consistent with an electron transfer process from the conduction band of the Si nanocrystals to the redox levels of the quenchers.

225.
EFFECTS OF FRAMEWORK STRUCTURE ON THE PHASE STABILITY OF MESOPHASE SILICA/SURFACTANT COMPOSITES. **A. F. Gross,** E. J. Ruiz, and S. H. Tolbert, Dept of Chemistry and Biochemistry, University of California, Los Angeles, Los Angeles, Ca 90095

Real time X-ray powder diffraction is used to examine kinetic effects and structural stability of hexagonal mesophase silicas formed by the cooperative reaction of silicate with a C-20 quaternary ammonium surfactant. Changing the amount of base in the synthesis alters the silica polymerizations which result in modified composite wall structures. Framework stability is investigated by forcing a temperature induced non-isothermal, hydrothermal, hexagonal to lamellar phase transition. The transition appears to be driven by a thermally induced change in surfactant packing. By following the phase transitions in composites made under different conditions with XRD, we find the activation energies of transformation as well as the Avrami n-parameter (that provides insight into the mechanism of this rearrangement). The data is used to look for correlations between the makeup of the structure and hydrothermal phase stability.

226.
ALIGNMENT AND ISOLATION OF SEMICONDUCTING POLYMER IN THE NANO-PORES OF AN ORDERED SILICA MATRIX. **J. Wu,** A. F. Gross, S. H. Tolbert, Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California, 90095

The semiconducting polymer MEH-PPV is incorporated into the pores of an oriented, ordered, mesoporous silica matrix. The matrix is synthesized from a silicate/surfactant liquid crystal which was aligned in a magnetic field. Silylation is used to optimize the interaction between the polymer and the silica host. The degree of alignment and confinement of the polymer are studied using polarized fluorescence spectroscopy. By combining fluorescence anisotropy data with 2-D X-ray diffraction data, it is possible to calculate the physical location of the polymer molecules using a simple geometric model. We conclude that as much a 80% of the incorporated polymer is isolated within the pores of the silica matrix. The incorporate polymer appears to be protected from oxidation; after intentional oxidation, fluorescence anisotropy indicates that virtually all of the optically active polymer is isolated within the silica framework.

227.
HIGH PRESSURE EFFECTS ON ORDERED SURFACTANT/INORGANIC MESOPHASE COMPOSITES. **J. Wu,** X. Liu, S. H. Tolbert, Department of Chemistry and Biochemistry, University of California at Los Angeles, Los Angeles, California, 90095

Surfactant templated mesophase silicas with long range hexagonal periodicity (MCM-41) are subjected to hydrostatic pressure up to 16 GPa in a diamond anvil cell. X-ray diffraction data indicate that the composites shows unusually high mechanical strength with compressibility close to that of bulk amorphous silica up to about 8 GPa in an argon medium. This result is surprising in light of the silica wall structure, which is less than 15 angstroms thick. Above 8 GPa, the silica matrix collapses inelastically, possibly caused by the concentration of water or argon into the pores. The observed high pressure effects depends on various factors including hydrostatic pressure medium, sample preparation, etc. Phase transitions under hydrothermal conditions are also studied under high pressure in the diamond cell. The effect of pressure on the phase transition kinetics is probed.

228.

SPECTROSCOPIC CHARACTERIZATION OF CdS NANOPARTICLES WITH DIFFERENT CAPPING ENVIONMENTS . **Bingsuo ZOU,** Reginald Little, Jianping Wang and Mostafa A. El-Sayed, School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, GA 30332

CdS nanoparticles in AOT reverse micelle has been chemically capped with ZnS, Cd(OH)2 and CdO. Absorption, flourescence spectra have been used to study the excitonic state, deeptrap state, quantum confined levels as the capping substance and thickness changes. Experimental results indicate that CdS nanoparticles in AOT reverse micelle can interact strongly with surfactan molecules. ZnS and Cd(OH)2 capping with 5 layer can confine carrier within CdS nanoparticles, however, their cappings depend on the particle sizes, interface charge balance and lattice mismatch. CdO capping layer trap carriers from CdS nanoparticles. The different capping behaviors of above substances originate from their bandgaps and chemical characteristics.

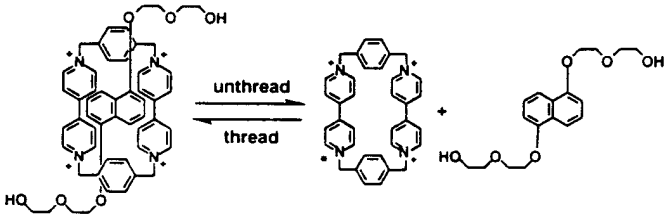
229. In-Situ Probing by Fluorescence Spectroscopy of the Formation of Continuous Highly-Ordered Lamellar Phase Mesostructured Thin Films

Michael H. Huang, Bruce S. Dunn, Hermes Soyez, and Jeffrey I. Zink, Departments of Chemistry and Biochemistry and Materials Science and Engineering, University of California, Los Angeles, California 90095

Continuous highly-ordered mesostructured lamellar phase thin films are formed by a dip-coating process from a sol consisting of tetraethoxysilane and the surfactant sodium dodecyl sulfate (SDS). X-ray diffraction patterns give sharp peaks extending to 14 orders, indicative of a highly-ordered structure with a lattice spacing of 37.9 Å. Film thickness is measured in real time by using interferometry; interference fringes remain constant in height above the sol on the continuously moving silicon substrate. In-situ fluorescence spectra of probe molecules were recorded to trace both the formation of the micelles and the solvent composition of the films as they are pulled in real time. Micelles are formed, break up, and reform to produce the final structure in 12 seconds.

230. A SUPRAMOLECULAR MACHINE IN THE SOLID STATE. Shinye Chia, Jeffrey I. Zink, and J. F. Stoddart, Department of Chemistry and Biochemistry, UCLA, Los Angeles, CA 90095

The threading/unthreading of the pseudorotaxane (1,5-bis-[(2-(2-(2-hydroxy)ethoxy)ethoxy]naphthalene and cyclophane) has been well stud'ed in solution. The photo-excitation and consequent oxidation of 9-anthracenecarboxylic acid effects the reduction of the cyclophane, inducing the unthreading of the pseudorotaxane.



By monitoring the fluorescence of 1,5-bis-[2-(2-(2-hydroxy)ethoxy)ethoxy]naphthalene, the redox cycle and thus the threading/unthreading of this system may be studied. We study this system in the sol-gel matrix and show that this process is uninhibited by the motion-restrictive media.

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The objective of the symposium on the Physical Chemistry of Sol-Gel Materials was to bring together scientists from the sol-gel field with physical chemists whose interests extend to sol-gel science. The symposium generated considerable response from the two communities. A total of six sessions were held in which there were 32 oral presentations along with a poster session with 24 papers. This symposium, sponsored by the Physical Chemistry Division of the American Chemical Society, was the first one to be directed at the underlying physical chemistry of the sol-gel field. The symposium covered those areas where physical chemistry has had a significant impact. Structural development, local chemistry and bonding, ion and molecular transport, confinement effects, dynamics and intramolecular properties are some of the topics covered during the six sessions.

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